

pheres having a density of 0.4 gm/cm³.

Chemically, cenospheres consist essentially of the following components by weight SiO₂ (55—61%) and Al₂O₃ (26—30%), with smaller quantities of Fe₂O₃ (2—10%), CaO (0.2—0.6%), MgO (1—4%), and Na₂O, K₂O (0.5—4.0%). By their high content of Al₂O₃, they differ distinctly in composition from commercial glass microspheres.

Prior researchers have studied the behaviour of syntactic foams comprising epoxy resin-bonded cenosphere structure under hydrostatic pressure. This material was proposed for use as a buoyancy material in deep submersible vehicles. Some preliminary pressurization experiments on these syntactic foams were carried out and suggested that cenospheres will probably perform as well as the manufactured microspheres for at least some applications.

Although epoxy resin-bonded cenospheres had yielded structures which combined low density (0.4 to .83 g/cm³) with high compressive strength, they contained three parts by weight of the epoxy resin for two parts by weight of the cenospheres. When subjected to intense heat, composites with such high resin contents will still give up toxic fumes and are likely to disintegrate.

In search for an inorganic cement to re-

place the organic polymer, we found that phosphoric acid would serve as this binder when mixed with cenospheres. After gradual heating of these premolds the mixed mass yields lightweight, rigid inorganic specimens of good structural integrity.

It is believed that the cementing of the cenospheres is effected by formation of chemical bonds between the phosphoric acid and the aluminum oxide in the cenospheres under elimination of water molecules, viz.,



This scheme is substantiated by the fact that only natural cenospheres, but no synthetic microballoons, can be effectively welded together by phosphoric acid, since the synthetic microballoons do not contain Al₂O₃ in their chemical composition.

In preliminary tests, structure with a density as low as 0.24/cm³ could be made with cenospheres produced by Fillite Ltd., England, and with a density of 0.48g/cm³ with water-floated cenospheres from West Virginia, U.S.A. Data on compressive strength of a few samples, together with the temperatures to which they had been heated, are shown in the following table:

SAMPLE	PREPARED AT °C	DENSITY g/cm ³	COMBINED STRENGTH Kg/cm ²
Fillite Cenospheres	200	.40	41
Fillite Cenospheres	950	.37	23
Cenospheres from West Virginia, Water-floated	200	.49	29
Cenospheres from West Virginia, Water-floated	950	.48	17
Cenospheres from West Virginia, Untreated	200	.72	64
Cenospheres from West Virginia, Untreated	950	.66	31

According to the present invention there is provided an inorganic composition that forms a rigid monolithic lightweight mass upon application of external heat; said composition comprising cenospheres separated from the fly ash formed when pulverized coal is burned, and phosphoric acid.

The composition may also comprise a source of metal ions. As discussed below, where hygroscopic properties are no problem,

cenospheres and phosphoric acid alone may be used to produce the composition.

The present invention also provides an inorganic composition that forms a rigid monolithic lightweight mass upon application of heat, said composition consisting essentially of a liquid binder comprising phosphoric acid, a source of metal ions and sufficient water to form a solution of metal phosphate and free phosphoric acid, and cenospheres separ-

ated from fly ash formed when pulverized coal is burned.

The metal ions produce metal phosphate in the binder liquid. Metal phosphate can be produced *in situ* during the preparation of the binder liquid or can be obtained from conventional sources of commercial metal phosphates.

In a further aspect the present invention also provides a method of bonding cenospheres to produce a rigid, lightweight material, comprising the steps of mixing spheres separated from fly ash with a liquid binder containing phosphoric acid to produce a moldable paste; molding the paste into a mass having a desired physical configuration; and heating the molded mass to a temperature below that temperature at which sintering of the cenospheres occurs.

In practice the present invention provides a lightweight inorganic material that is fire-proof and which shows considerable promise as an insulating material for building and construction purposes. The composition of the present invention is commercially desirable utilizing cenospheres produced as a waste by-product in coal-fired electrical generating plants and similar installations.

It has been known for years that a small proportion of the particles in pulverized-coal ash consists of thin-walled hollow spheres commonly termed "cenospheres". The apparent density of these fly ash cenospheres is less than that of water. They separate from the dense ash in settlement lagoons. Different amounts of the lightweight cenospheres are produced by the boilers at different power stations. In some cases the quantity of ash cenospheres is negligible. Other boilers discharge sufficient amounts of cenospheres to form a thick layer of floating material on lagoons. The amount of cenospheres is influenced by the nature of the mineral matter in the coal being fired and the method of fly ash selection and disposal.

The following constitutes a brief summary of the properties of cenospheres:

- a. Cenospheres average 20 to 200 microns in diameter and are regular spheres with coherent, non-porous shells of silicate glass. The thickness of shell is about 10% of the radius. The true particle density of the individual spheres is in the range of 0.4 to 0.6 g/cc and the bulk density 0.25 to 0.40 g/cc.
- b. The floating spheres collected from lagoons are free from soluble matter.
- c. The hollow spheres start to sinter at 1200°C. and collapse above 1300°C.
- d. The gas in the cenospheres consists mainly of CO₂ and H₂. At room temperature, the internal pressure is 0.2 atmos.
- e. The cenospheres are formed at an estimated temperature of 1400°C. and the formation and size are governed by the

viscosity and surface tension of the fused silicate glass, by rate of change in particle temperature and the rate of diffusion of gases in the silicate. The molten spheres freeze at 1000°C. trapping the gases which are formed internally through the catalytic action of ferric oxide or carbonaceous material present.

- f. The chemical composition of cenospheres is somewhat variable but the principal constituents are aluminum, silicon and oxygen. The range of chemical composition (percent) by weight as follows:

Silica (as SiO ₂)	55 to 61	
Alumina (as Al ₂ O ₃)	26 to 30	
Iron Oxides (as Fe ₂ O ₃)	2.0 to 10	
Calcium (as CaO)	0.2 to 0.6	
Magnesium (as MgO)	1.0 to 4.0	85
Alkalies (as Na ₂ O, K ₂ O)	0.5 to 4.0	
Loss on ignition	0.01 to 2.0	80

It is obvious from the foregoing composition that a cenosphere is a glassy matrix of calcined clay in which the gases have had no opportunity to escape.

Some generating plants discharge sufficient quantities of fly ash cenospheres to form a thick layer of floating material on lagoons. The floaters may create a significant air pollution problem, since on a warm day the top surface can dry and be blown away. Given favorable raw material and environmental conditions during combustion, one can expect as much as 4 to 5% by weight, or, on a volume bases, as much as 15 to 20% of the fly ash to consist of cenospheres.

In comparison to the dense fly ash material, the silica content of the cenospheres is higher, but the calcium oxide content is lower. Cenospheres also contain a small amount (0 to 2% by weight) of soluble material, in contrast with two to five percent by weight of soluble material in precipitated fly ash.

Observations under optical and electron microscopes have shown that fly ash cenospheres are colorless glass spheres of sizes ranging from 20 to 200 microns. There is a noticeable absence of small particles, less than 10 microns in diameter, commonly found in dense fly ash, excluding the usual small amount of debris from broken spheres. The cenospheres do have a demonstrated absence of pores on their surfaces. Blisters are occasionally seen on large particles.

The separation of dried cenospheres into different size fractions by sieving is much easier than with precipitated fly ash. The absence of the sub-micron particles prevents the formation of agglomerates and clogging of sieves. Cenospheres are much larger than the particles of dense precipitated fly ash from a given station. For example, floating ceno-

spheres contain only five percent by weight of particles that are less than 50 microns in diameter, wherein dense precipitated fly ash might have more than 80% below this size.

The behaviour of cenospheres at high temperatures has been observed by heating in a microscope. Published reports state that no change in size or in shape of the cenosphere occurs up to approximately 1250°C. Above this temperature the size of the particles slowly decrease, and at 1300°C. they collapsed to a dense blob. Cenospheres from several sources were tested and it was found that they all collapsed at approximately the same temperature.

The collapse without expansion or sudden gas release suggests that either there was a partial vacuum in the particles or that the diffusion of gas in the particle shell was sufficiently rapid to prevent increase of internal pressure on heating. A rapid collapse of particles took place when these were inserted in a furnace at 1400°C.

On sintering there has been observed a marked difference in cenospheres in comparison with dense precipitated fly ash. Pellets made of cenospheres require heating to 1200°C. before a bond by sintering occurs. Dense precipitated fly ash starts to sinter at 1000°C. to 1100°C. and there is no significant change of volume during sintering. The high sintering temperature of fly ash cenospheres is probably due to the absence of sub-micron particles, and perhaps also to the fact that some of the low melting glass is dissolved during separation of cenospheres from the dense ash by flotation in water. Another possible explanation is that the stable cenospheres form only from the silicates of a higher softening temperature.

These cenospheres are the starting material for a lightweight and fireproof material which is capable of replacing plastic foam in many applications, particularly as an insulating material for building and construction purposes. Tests of this material have shown it to be stable at temperatures as high as 2000°F. It will simply not burn because of its totally inorganic nature. Furthermore, the material can be produced inexpensively from the waste by-product cenospheres. The material is believed to be an economic substitute for plastic in the manufacture of ceiling and wall tiles, door cores, insulation, trims and molding.

We have found that we can bond cenospheres with phosphoric acid plus various metal phosphates. The ones tested and shown to be satisfactory are aluminum, zinc, magnesium and chromium. Other metal phosphates are also satisfactory. The cenospheres can be bonded by using only phosphoric acid but this produces a very hygroscopic product. The metal phosphates seem to prevent this hygroscopicity.

The optimum amount of the acid-phosphate mix appears to be in the range of 1 part by weight acid mix to 0.5 to 3.5 parts of cenospheres. The acid-phosphate mix composition depends upon the individual metal phosphate as some of them are not very soluble in phosphoric acid. In all cases, the metal phosphates have been made *in situ* by adding a suitable oxide, hydroxide or carbonate to the acid. There is no reason however, to preclude the use of commercial metal phosphates if they are available. The range of molar ratios of metal phosphates to free phosphoric acid is from 0.1/1 to 1/1.

The times and temperatures of curing the premolds of binder and cenospheres can be varied from 3 hours at 500°C. to 48 hours at 600°C. and even to 3 hours at 700°C. but the optimum time and temperature seems to lie between 8 and 24 hours at 600°C. Heating the premolds to temperatures in the range 200 to 950°C. yields specimens of great structural integrity. Compressive strengths generally are about 750-800 pounds per square inch but values up to 1500 psi have been obtained.

Example 1.

The binder liquid was prepared by adding $\text{Al}(\text{OH})_3$ and H_2O to 85% by weight H_3PO_4 with heating to cause solution.

	Grams
H_3PO_4 (85% by weight)	384
$\text{Al}(\text{OH})_3$	78
H_2O	138

Thirty grams of the above binder solution was added to 90 grams of cenospheres. After careful mixing, the material was pressed into a mold, removed from the mold, and dried overnight at 80°-90°C. The dried, molded material was then heated to 60°C. for 8 hours and then cooled slowly.

Example 2.

A binder liquid of the following composition was prepared:

H_3PO_4 (85%)	354 Grams	110
$\text{Zn}(\text{OH})_2$	185 Grams	
H_2O	126 Grams	

The cenospheres were mixed with the binder liquid in the ratio of 3 parts by weight of cenospheres to 1 part by weight of binder liquid. The material was molded and dried as in Example 1. It was then heated for curing to 60°C. for 24 hours.

Example 3.

Binder Liquid	Grams	120
H_3PO_4 (85%)	317	
MgO	30	
H_2O	52	

phosphate are metal oxides, hydroxides or carbonates. The liquid binder may be in the form of a solution of metal phosphate, free phosphoric acid and sufficient water to form a solution of metal phosphate and free phosphoric acid. The solution is preferably a saturated solution of the metal phosphate in phosphoric acid.

5	Binder Liquid	Grams
	H_2PO_4 (85%)	384
	Al (OH) ₃	78
	Mg ₃ (PO ₄) ₂ · 5H ₂ O	30
	H ₂ O	138

WHAT WE CLAIM IS:—

1. A method of bonding cenospheres to produce a rigid, lightweight material, comprising the steps of mixing cenospheres separated from fly ash with a liquid binder containing phosphoric acid to produce a moldable paste; molding the paste into a mass having a desired physical configuration; and heating the molded mass to a temperature below that temperature at which sintering of the cenospheres occurs.

2. A method as claimed in claim 1 wherein the liquid binder further comprises a source of metal ions.

3. A method as claimed in claim 1 wherein the liquid binder is produced by adding to phosphoric acid a metal oxide, hydroxide or carbonate as a source of metal phosphate in the liquid binder, the molar ratio of metal phosphate to free phosphoric acid in the liquid binder being between 0.1/1 and 1/1.

4. A method as claimed in claim 1 wherein the liquid binder further comprises a source of metal ions, the liquid binder comprising a solution of metal phosphate in free phosphoric acid, the molar ratio of metal phosphate to free phosphoric acid in the liquid binder being between 0.1/1 and 1/1.

5. A method as claimed in claim 4 wherein the liquid binder is mixed with the cenospheres in a proportion by weight of one part liquid binder to 0.5 to 3.5 parts cenospheres.

6. A method as claimed in claim 1 wherein the molded mass further comprises an organic powder or beads of a material that volatilizes during the heating step.

7. A method as claimed in claims 1 through 5 wherein the molded mass further comprises a material that foams during the heating step.

8. A method as claimed in claims 1 through 5 wherein the molded mass further includes fly ash as an inorganic filler.

9. A method as claimed in claims 1 through 8 wherein the temperature to which the molded mass is heated in the range of 200—950°C.

10. An inorganic composition that forms a rigid monolithic lightweight mass upon application of external heat; said composition comprising cenospheres separated from the fly ash formed when pulverized coal is burned, and phosphoric acid.

11. A composition as claimed in claim 10, further comprising a metal phosphate. 125

12. A composition as claimed in claim 10,

wherein the molar ratio of metal phosphate to free phosphoric acid is between 0.1/1 and 1/1.

- 5 13. A composition as claimed in claim 10,
further comprising a metal phosphate, the
range of molar ratios of metallic phosphate
to free phosphoric acid being 0.1/1 to 1/1.
- 10 14. A composition as claimed in claim
13 wherein the ratio by weight of metal phos-
phate and free phosphoric acid to cenospheres
is in the range one part of metal phosphate
and free phosphonic acid to 0.5 to 3.5 parts
of cenospheres.
- 15 15. The product which results after heating
a composition as claimed in any one of claims
10 to 14 to a temperature in the range of
200—950°C. for a period of 3 to 48 hours.
- 20 16. An inorganic composition that forms
a rigid monolithic lightweight mass upon appli-
cation of heat, said composition consisting
essentially of a liquid binder comprising phos-
phoric acid, a source of metal ions and suffi-
cient water to form a solution of metal phos-
phate and free phosphoric acid, and ceno-
spheres separated from the fly ash formed
when pulverized coal is burned.
- 25 17. A composition as claimed in claim 16

18. A composition as claimed in claims 16 and 17 wherein the ratio by weight of liquid binder to cenospheres is in the range of one part of liquid binder to 3.5 parts of cenospheres. 35

19. The product which results after heating a composition as claimed in any one of claims 16 to 18 to a temperature in the range of 200—950°C. for a period of 3 to 48 hours.

20. A product as produced by the method claimed in any one of claims 1 to 9.

21. The method of producing the composition claimed in claims 10 through 19 and as described and set out herein.

22. A method of producing a lightweight composition as set forth in any of the foregoing Examples.

23. The composition produced by the method as claimed in claim 22.

**WASHINGTON STATE UNIVERSITY
RESEARCH FOUNDATION, INC.**

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